



# Starch-based bio-elastomers functionalized with red beetroot natural antioxidant



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## ABSTRACT

Red beetroot (RB) powder was incorporated into starch-based bio-elastomers to obtain flexible biocomposites with tunable antioxidant properties. Starch granules within the bio-elastomers affected the release of the antioxidant molecule betanin in the RB powder. The bio-elastomers were hydrophobic and resisted dissolution in water, hence the release of betanin was due to diffusion rather than polymer matrix disintegration. Hydrophobicity was maintained even after water immersion. Released betanin demonstrated highly efficient antioxidant scavenging activity against 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH<sup>•</sup>) and 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) radical cation (ABTS<sup>•+</sup>). RB powder was also found to increase the Young's modulus of the bio-elastomers without compromising their elongation ability. Infrared spectral analysis indicated weak interactions through hydrogen bonding among starch granules, RB powder and PDMS polymer within the bio-elastomers. Hence, as a simple but intelligent biomaterial consisting of mainly edible starch and RB powder the present bio-elastomers can be used in active packaging for a variety of pharmaceutical, medical, and food applications.

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## 1. Introduction

Starch is one of the most abundant natural resources and has been used as a promising material in the production of green plastics due to its low cost, renewability and biodegradability (Fan et al., 2015; Tang & Alavi, 2011). In fact, several starch-based thermoplastics mainly developed for food packaging are commercially available today (Privas, Leroux, & Navard, 2013; Tang & Alavi, 2011; Wu & Hakkarainen, 2014). However, a number of drawbacks such as poor waterproof properties, brittleness, low tensile strain and lack of thermal stability hinder further applications of thermoplastic starch (Fan et al., 2015; Privas et al., 2013; Zhang et al., 2013). The common approach to overcome these disadvantages is to blend unmodified or thermoplastic starch with other synthetic or natural polymers (Xu, Canisag, Mu, & Yang, 2015). For instance, blending thermoplastic starch with various polyesters (Tang & Alavi, 2011) resulted in commercial products (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008; Walker, Tao, & Torkelson, 2007). Moreover, unmodified starch has also been compounded into a number of resins and polymers such as polyethylene

(Walker et al., 2007), polyacrylamide (Fan et al., 2015), cyanoacrylates (Kim & Peterson, 2012), and very recently into silicone polymers (Ceseracciu, Heredia-Guerrero, Dante, Athanassiou, & Bayer, 2015).

Recently, food industry has shown great interest towards the concept of bioactive, smart and edible packaging materials (Schieber, Stintzing, & Carle, 2001; Siracusa et al., 2008; Wu et al., 2013). Particularly, bio-based smart food packaging materials that can sense and delay food spoilage due to oxidation is at the top of the list (Akhtar et al., 2012; Pokorny, Yanishlieva, & Gordon, 2001; Tran et al., 2016). The advantage of adding antioxidants to packaging material instead of putting them directly into food is the controlled and gradual release of the antioxidants during food storage, rather than delivering them in a single massive dose (Akhtar et al., 2012; Iñiguez-Franco et al., 2012; Pokorny et al., 2001). Furthermore, in order to achieve a specific food shelf life, smaller amounts of antioxidants in the form of additives in packaging materials will be sufficient rather than larger amounts in food, which can interfere with taste and other sensory-related properties (Stintzing & Carle, 2007; Tang & Alavi, 2011). Natural antioxidant products are prefer compared to synthetic one since it is safer, easier to market and can have various human health benefits as well (Akhtar et al., 2012; Schieber et al., 2001; Sonkaew, Sane, & Suppakul, 2012). For instance, natural antioxidants of green

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tea (Wu et al., 2013), citrus (Tongnuanchan, Benjakul, & Prodpran, 2012), curcumin (Sonkaew et al., 2012), and berries have been shown to be very effective in scavenging free radicals and subsequently they can delay both the deterioration of foods and the damage of human tissues.

Red beetroot (RB) is a commonly consumed vegetable for cooking in daily life. RB contains high concentration of betalains, mostly Betanin (E162) (Stintzing & Carle, 2007), that are used as food colorants and food additives in beverages, candies, dairy and cattle products (Esatbeyoglu, Wagner, Schini-Kerth, & Rimbach, 2015; Ravichandran et al., 2013; Wettasinghe, Bolling, Plhak, Xiao, & Parkin, 2002). Water soluble betalain pigments possess several desirable biological activities including antiradical, antioxidant, anti-inflammatory, hepatoprotective, against human lung cancer and antitumor properties at low concentrations (Cai, Sun, & Corke, 2005; Ravichandran et al., 2013; Wootton-Beard & Ryan, 2011). In addition, valorization of processed RB waste or overstock RB powder is of interest due to potential cost reductions and waste minimization in food industry (Schieber et al., 2001). In a recent work (Ceseracciu et al., 2015), we have demonstrated the development of robust and biodegradable elastomers by incorporating large amounts of unmodified corn starch granules (up to 80%) into polydimethylsiloxane (PDMS) matrices, which showed excellent mechanical stress relaxation and energy dissipation properties. In the present work, we aim to functionalize these bio-elastomers with RB powder as a natural and low cost antioxidant source to prepare smart biomaterials having efficient antioxidant properties that can potentially be used in food packaging applications. The release of water soluble antioxidant from the bio-elastomers as well as its free radical scavenging activity was systematically evaluated. Furthermore, detailed experimental work is presented in order to characterize mechanical, morphological, wetting and water uptake properties.

## 2. Experimental section

### 2.1. Materials

RB powder was kindly provided by a local food processor, IDA S. R.L, Italy. Silicone precursor (Elastosil E43) was obtained from Wacker Chemie AG, Germany. Corn starch, 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), potassium persulfate, betanin, ethanol, formic acid and acetonitrile were purchased from Sigma-Aldrich. All chemicals were analytical grade and used as received without any further purification. Deionized water was obtained from Milli-Q Advantage A10 ultrapure water purification system.

### 2.2. Preparation of the antioxidant films

The antioxidant bio-elastomer films were prepared by a simple mixing process and casting into a mold. Depending on the starch and red beetroot (RB) content, all the samples were denoted as P.S.R x/y/z, where, P, S and R stand for PDMS, starch and RB components in the bio-elastomer films and x, y and z are the weight percentages of PDMS, starch and RB in the bio-elastomer, respectively. Table 1 presents the details of the formulations and designation of the bio-elastomers. For instance, the preparation of P.S.R 30/60/10 bio-elastomer is as follows: RB (1 g) and corn starch (6 g) were added in heptane (14 mL) to obtain mixture with concentration of 50 % w/v. To ensure homogenous dispersion, the mixture was sonicated for one minute using a 500 W probe sonicator (VC 505, Sonics & Materials Inc.) at 40% amplitude. The sonicated mixture was then stabilized for 10 min to let it cool to

**Table 1**  
Formulation and designation of the prepared samples.

Series	Samples	% wt		
		PDMS	Strach	RB
P.S.R 30 (Films with 30% of PDMS)	P.S.R 30/70/00	30	70	0
	P.S.R 30/68/02	30	68	2
	P.S.R 30/66/04	30	66	4
	P.S.R 30/64/06	30	64	6
	P.S.R 30/62/08	30	62	8
P.S.R 50 (Films with 50% of PDMS)	P.S.R 30/60/10	30	60	10
	P.S.R 50/50/00	50	50	0
	P.S.R 50/48/02	50	48	2
	P.S.R 50/46/04	50	46	4
	P.S.R 50/44/06	50	44	6
	P.S.R 50/42/08	50	42	8
	P.S.R 50/40/10	50	40	10

room temperature. Subsequently, silicone resin (Elastosil E43) (3 g) was added to the mixture and vigorously stirred for about 5 min to obtain a homogenous blend. Finally, the mixture was poured onto a square Petri dish (120 × 120 mm) and dried under an aspirated hood. After 24 h, the bio-elastomer film was removed from the Petri dish and allowed to dry and crosslink for another 24 h period. The thickness of the films was measured to be approximately 390 ± 40 μm. The thickness of the films containing 30% (P.S.R 30) and 50% of PDMS (P.S.R 50) were 421 ± 19 μm and 364 ± 21 μm, respectively. The increase of 20% starch content led to approximately 60 μm difference in film thickness due to the difference in film density. Detailed thickness measurement data as a function of RB content is shown in Fig. S1 (Supporting Information).

### 2.3. Characterization of the films

#### 2.3.1. Chemical analysis

The chemical compositions and potential intermolecular interactions within the films were characterized by an attenuated total reflectance (ATR) accessory (MIRacle ATR, PIKE Technologies) coupled to a Fourier transform infrared (FT-IR) spectrometer (Equinox 70 FT-IR, Bruker). The measurements were conducted within 4000–600 cm<sup>-1</sup> range with a resolution of 4 cm<sup>-1</sup> and 128 repetitive scans averaged for each spectrum. At least triplicate measurements were performed for each sample.

#### 2.3.2. UV-Vis measurements

UV-visible spectroscopy was used to determine the absorption of solutions. All the solutions were kept in a PMMA plastic cuvette (1.5 mL capacity) that was placed in a Varian CARY 300 Scan UV-Vis spectrophotometer sample holder. The UV absorbance measurements were carried out in the wavelength range of 200–800 nm.

#### 2.3.3. Morphological characterization

The surface morphology of the films was investigated by Scanning electron microscopy (SEM), using a variable pressure JEOL JSM-6490LA microscope equipped with a tungsten thermionic electron source working in high vacuum mode, with an acceleration voltage of 20 kV. The samples were previously mounted on stubs and then sputter coated with a 10 nm gold layer using a Cressington 208HR high resolution sputter coater (Cressington Scientific Instrument Ltd, U.K.). Imaging was obtained with secondary electrons.

#### 2.3.4. Moisture uptake

The bio-elastomer films were previously dried in vacuum for 24 h. After that, pre-weighted (m<sub>1</sub>) 2 × 2 cm<sup>2</sup> samples were kept

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